STUDIES ON BIMOLECULAR ALKALOIDS. PART I. ON DISINOMENINE AND ψ-DISINOMENINE.

By Kakuji GOTO and Hideo SUDZUKI.

Received March 25, 1929. Published May 28, 1929.

The milder action of oxidising agents, such as $AuCl_3$, $AgNO_3$, $K_3Fe(CN)_6$, $KMnO_4$, $FeCl_3$ and H_2O_2, on sinomenine leads to the formation of two isomeric, bimolecular substances, disinomenine and ψ-disinomenine in a nearly equal proportion. These two alkaloids are very similar in their behaviour, but are distinguished by the following characteristics.

	Disinomenine	ψ-Disinomenine
M. p. of free base	222°	227°
Dec. p. of free base	245°	243°
Crystal form	plates	hairy needles
M. p. of hydrochloride	>290°	>290°
Solubility of hydrochloride	0.6%	∞
Dec. p. of methiodide	263°	268°
M. p. of oxim	265° (dec.)	>290°
M. p. of semicarbazone	>290°	>290°
$[\alpha]_D$	+149.98°	−127.03°
Formaldehyde-H_2SO_4	pink	yellow

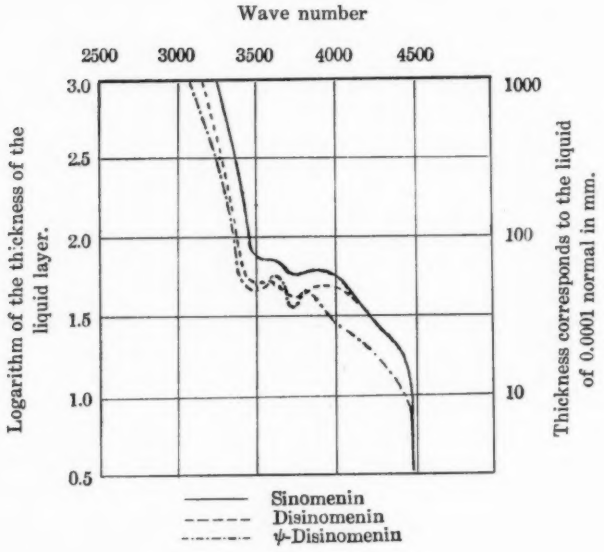
The acetolysis of the two substances gives the identical tetraacetyl-disinomenol, which is converted into the identical tetramethoxy-, tetraethoxy- and tetrabenzoyl-derivatives respectively, and these derivatives of disinomenol are again quite identical with those prepared from disinomenol, obtained by the linking together of sinomenol by the action of boiling 66% potash.[1]

Thus, the two new alkaloids seems to be stereoisomeric, but not enantiomorphic, since they are quite easily separated from each other by the recrystallisation of their hydrochlorides. The isomerism here may have been caused by the difference in the third nucleus of phenanthrene, i.e. perhaps by the difference in the linking position of the ethanamine chain. Spectrographic study gives little clew in this respect, the curve of the absorption of ψ-disinomenine being almost identical with that of disinomenine.

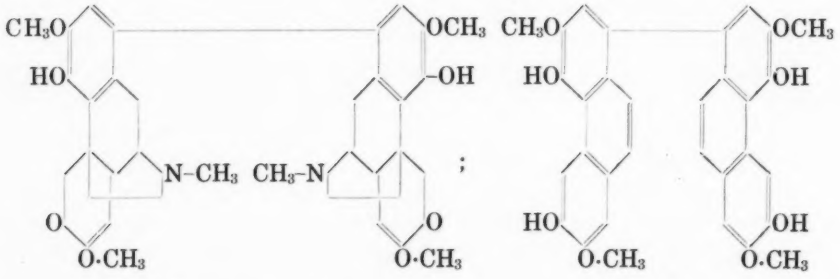
As regard to the linking position of two sinomenine molecules in these substances, the position 2, opposite to the free phenolic hydroxyl may be

see errata V.4, P 298

(1) See *Proc. Imp. Acad.*, **2** (1926), 414.



assumed with some certainty from the following two facts. In the first place, the strong diazoreaction of sinomenine (sensitiveness 1:2,000,000) is greatly diminished in these two substances (1:50,000). Secondly, the monobrom-sinomenine, in which the diazoreaction is similarly diminished (1 : 50,000) and on that account the bromine atom seems to occupy the position 2, does not give a bimolecular substance by the same oxidising agent and treatment.



Disinomenine occurs in nature, accompanying sinomenine, but ψ-disinomenine has not been isolated from sinomenium acutum up to present.

Experimental.

Preparation of Disinomenine and ψ-Disinomenine. *With potassium ferri-cyanide and sodium carbonate.*—Potassium ferricyanide solution (1 mol.; 10.5 gr. in 300 c.c. water) is poured into an aqueous solution (300 c.c.) of sinomenine hydrochloride (12 gr.; 1 mol.) at 50°. The mixture is immediately made alkaline with sodium carbonate solution. The precipitates, richly formed, are collected on a filter-paper and after being washed with water, redissolved in a small quantity of dilute hydrochloric acid. After standing overnight, the hydrochlorides of disinomenine and ψ-disinomenine are deposited. By repeated crystallisation from water, the hydrochloride of disinomenine can be obtained in a pure state. From the united filtrates, the free base of ψ-disinomenine can be precipitated by ammonia, and recrystallised from methyl alcohol.

With silver nitrate. Free base of sinomenine (9 gr.) is dissolved in alcohol (100 c.c.) and water (200 c.c.) and is oxidised by silver nitrate (7 gr.) in aqueous solution (300 c.c.) The isolation of the bases, after the removal of metallic silver and silver ion, is carried out in the almost same way as above.

Properties of disinomenine.—Hexagonal plates from methyl alcohol (solubility 1:50 hot; 1:250 cold.) M. p. 222° and decomposes at 245°. With formaldehyde sulphuric acid, it takes a pink colour.

Anal. Found: C=70.07, 69,03; H=6.85, 6.89; N=4.69, 4.63%. Calc. for $(C_{19}H_{22}NO_4)_2$: C=69.68; H=6.47; N=4.28%.

Mol. wt. Found: (in glacial acetic acid) 670, 677; (in boiling acetone) 659. Calc. for $(C_{19}H_{22}NO_4)_2$: 656.

Hydrochloride: m. p. >290° (Cl=9.64, 9.66. Calc., 9.65%.)

Solubility in cold water: 0.6%; in boiling 3.3%.

Methiodide: m. p. 263° (dec.). Long prisms from water (solubility, 0.3%.)

Oxim: m. p. 265° (dec.).

Semicarbazone: m. p. >290°.

Properties of ψ-Disinomenine. Long hairy needles from methyl alcohol. It dissolves easily in cold methyl alcohol, but when once these hairy needles containing methyl alcohol are formed, it becomes as difficultly soluble as disinomenine. M. p. 228°, decomposing at 245°. In formaldehyde sulphuric acid, it dissolves with a yellowish brown colour.

Anal. Found: C=66.57, 66.99, 66.83; H=7.05, 6.56, 8.03; N=4.24%. Calc. for $(C_{19}H_{22}NO_4)_2+2CH_3OH$: C=66.66; H=7.02; N=3.78%.

Mol. wt. Found: (in glacial acetic acid) 696. Calc. for $(C_{19}H_{22}NO_4)_2$: 656.

Methoidide: Polyhedral crystal from water. M. p. 267~268° (dec.) (Found: I=26.83. Calc.: I=27.02%).

Oxim: m. p. >280°. (Found: N=7.76. Calc. for dioxim: N=8.16%).

Semicarbazone: m. p. <290°.

Acetolysis of Disinomenine and ψ-Disinomenine. Disinomenine (1 gr.) is heated with acetic anhydride (5 gr.) in a sealed tube at 180° for 8 hours. The contents are poured into water and the acetic anhydride is destroyed by boiling. The insoluble part is recrystallised from benzene (15 gr.) The crude tetracetyl-disinomenol thus obtained, amounts to 0.2 gr. and already melts at 253°. It is once more recrystallised for analysis.

The same treatment of ψ-disinomenine gives the identical tetracetyl-disinomenol.

Anal. Found: C=67.78; H=4.91%. Calc. for $C_{40}H_{34}O_{12}$: C=67.98; H=4.81%.
Mol. wt. Found: (by Rast's) 703. Calc. for $C_{40}H_{34}O_{12}$: 706.
Methoxyls. Found: 17.28%. Calc. for $4CH_3O$-: 17.56%.

Nitrogenous decomposition products were in both cases methyl-ethyl amine, as the case with sinomenine (Gold salt, m. p. 179°; Platinum salt, dec. p. 224°). Yield: 0.25 gr. as hydrochloride from 3 gr. of ψ-disinomenine, and 0.2 gr. from 3 gr. of disinomenine.

The acetyl groups are easily hydrolysed away by alcoholic sodium hydroxide, and, from the disinomenol thus formed, tetramethoxy-, tetraethoxy, and tetrabenzoyl-disinomenol can easily be prepared by the action of dimethyl- and diethyl-sulphate and benzoyl chloride respectively. In the following, these three derivatives were prepared from the tetracetyl-disinomenols obtained from disinomenine as well as from ψ-disinomenine.

Disinomenol: m. p. >310°. It takes a beautiful blue colour in an acetone solution, when oxidised by ammoniacal silver (Sensitiveness 1:50,000).

Anal. Found: C=70.24; H=5.21%. Calc. for $C_{32}H_{26}O_8$: C=71.37; H=4.83%.

Tetramethyl-disinomenol: m. p. 240°, Fine needles difficultly soluble in cold acetone.

Anal. Found: C=72.70; H=5.92%. Calc. for $C_{36}H_{34}O_8$: C=72.72; H=5.72%.
Mol. wt. Found: (by Rast's) 638. Calc. for $C_{36}H_{34}O_8$: 594.
Methoxyls. Found: 40.01%. Calc. for $8CH_3O$-: 41.75%.

Tetra-ethyl-disinomenol: m. p. 177° (184°, very pure specimen).

Anal. Found: C=74.10; H=6.64%. Calc. for $C_{40}H_{42}O_8$: C=73.84; H=6.46%.
Mol. wt. Found: (by Rast's) 624. Calc. for $C_{40}H_{42}O_8$: 650.
Methoxyls. Found: 18.70%. Calc. for $4CH_3O$-: 19.07%.

Tetrabenzoyl-disinomenol: m. p. 280°, long needles. Very difficultly soluble in ordinary solvents. Benzoylation of disinomenol can only be carried out smoothly in ethyl-benzoate solution by benzoyl chloride and aqueous sodium hydroxide. The same substance can be obtained by heating disinomenol (1 gr.) with benzoic anhydride (5 gr.) in a stoppered test-tube at 180°–200° for 6 hours.

Anal. Found: C=74.79; H=4.11%. Calc. for $C_{60}H_{42}O_{12}$: C=75.47; H=4.40%.
Mol. wt. Found: (by Rast's) 1010, Calc. for $C_{60}H_{42}O_{12}$: 954.

On Colour Reaction of Monomolecular and Bimolecular Phenanthrene. Sinomenol, 3,7-dimethoxy-4,6 dioxy phenanthrene, dissolves yellow in cold conc. sulphuric acid, but almost decolourised on the addition of water. On the contrary, disinomenol, bis-1,1′- (3,7-dimethoxy- 4,6-dioxy)-phenanthrene dissolves brown in cold conc. sulphuric acid, and gives intensely purple flocculations on diluting with water. The same behaviour was ascertained with dimethyl-, diethyl-, diacetyl- and dibenzoyl-derivatives of sinomenol and with corresponding tetravalent derivatives of disinomenol. This reaction can be utilised advantageously in the study of potash fusion of phenanthrene alkaloids, since some of them are expected to give rise to bimolecular phenanthrene derivatives in that treatment.

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THE DETERMINATION OF THE HELIUM CONTENT OF SOME JAPANESE MINERALS. II.

By Jirô SASAKI.

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On the minerals occurring in Japan, the determination of helium content was undertaken as a continuance of the former work.[1] The apparatus employed and so the method of extracting helium were the same as those described in the previous communication, special cares, however, sometimes having been taken for the sampling of the minerals. The results are given in the following table.

(1) This Bulletin, **1** (1926), 253; *Sci. Pap. Inst. Phys. Chem. Res.*, **5** (1927), 258.

Mineral	Locality	Sample taken gr.	Helium yielded c.c. at N. T. P.	Helium c.c. per gr. of Mineral	Helium %
Conglomerate of Samarskite and Columbite	Ishikawa in Fukushima	12.43	2.44	0.20	0.0035
Naegite	Naegi in Gifu	19.29	0.55	0.028	0.00051
Ilmenite	Korea	62.27	$<$0.028	0.00044	0.000008
Ilmenite	Chôhakumen in Korea	41.22	No He	—	—
Sphene	Ishikawa in Fukushima	22.34	0.12	0.0054	0.000098
Sphene	Mozumi in Gifu	19.20	No gas evolved	—	—
Rutile[1]	Mayuyama in Kagawa	26.31	$<$0.00014	0.0000053	0.000000095
Apatite	Kurokura in Kanagawa	46.91	Small quantity of gas evolved	—	—
Apatite	Kuropira in Yamanashi	63.28	Fair quantity of H_2 evolved	—	—
Tourmaline	Ishikawa in Fukushima	52.11	Small quantity of gas evolved	—	—
Axinite	Obira in Ôita	67.16	Small quantity of H_2 evolved	—	—

The rutile of Mayuyama and the ilmenite of Korea showed no radioactivity, while the sphene from Ishikawa was feebly radioactive. As to the conglomerate of samarskite and columbite from Ishikawa the amount of uranium was determined to be 4.0% U_3O_8 by the Brearley's method and that of thorium 0.036% ThO_2 by the hydrogen peroxide method.

The geological age of the above stated mineral resembling ånnerödite and that of naegite were computed by the same way as has been shown in the previous paper. The age of samarskite accompanying columbite in some extent was thus calculated as to be 100 million years from the foregoing results. For the amounts of uranium and thorium in naegite from Naegi, however, the author has used of the analytical results formerly obtained by Prof. Y. Shibata and K. Kimura[2] and has found them to be 2.69% UO_2 and 2.85% ThO_2. The age was found to be 17 million years. It showed a somewhat less value in comparison with the age of the fergusonite from the same district as has been given in the previous paper. This difference might probably be ascribed to the inequality of the amount of radioactive constituents contained in the two samples used by Prof. Y. Shibata and the author.

In conclusion, the author wishes to express his best thanks to Dr. S. Iimori for his kind advice and constant guidance; his thanks are also due to Mr. T. Yoshimura who was kind enough in supplying some of the samples to him.

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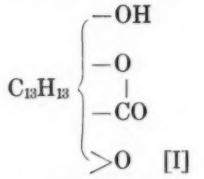
(1) The volume was measured under the reduced pressure.
(2) *J. Chem. Soc. Japan*, (in Japanese), **42** (1921), 1.

UEBER DIE KONSTITUTION DES NODAKENINS, EINES NEUEN GLUCOSIDS VON PEUCEDANUM DECURSIVUM MAXIM. II.[1]

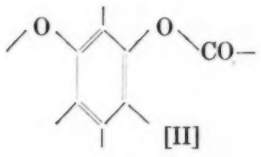
Von Junzo ARIMA.

Eingegangen am 20, April 1929. Ausgegeben am 28, Mai 1929.

In der vorigen Mitteilung[2] ist gezeigt worden, dass das Nodakenetin, das Aglykon des Nodakenins, das Formelbild (I) besitzt und in seinem Moleküle den Kern (II) enthält, und dass sein Verhalten gegen Alkalien dem der Cumarinreihen sehr ähnlich ist.



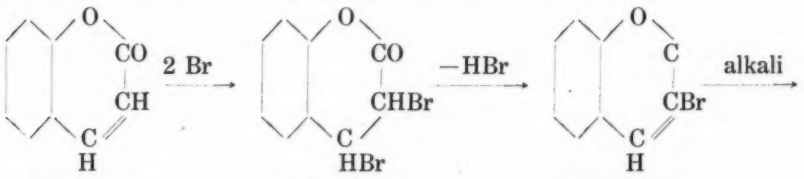
[I]



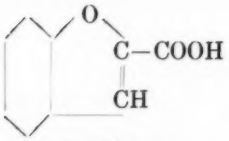
[II]

In dieser Mitteilung kann der Verfasser die weiteren Aehnlichkeiten des Nodakenetins mit den Cumarin-reihen beweisen.

Das Nodakenetin absorbiert 1 Mol. Brom unter Bildung einer Monobromverbindung, und diese Bromverbindung wird durch Erwärmen mit alkoholischem Alkali in eine einbasische Säure, die die Formel $C_{14}H_{14}O_5$ hat und ein Atom Sauerstoff mehr als das Nodakenetin enthält, die aber keine Lacton- oder Phenolhydroxyl-gruppe besitzt. Diese Reaktions-reihen sind den folgenden Reaktionen-reihen des Cumarins analog :



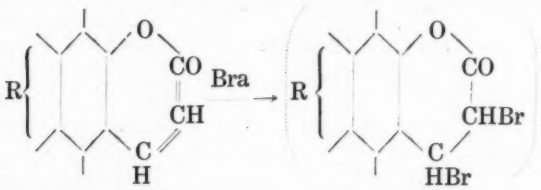
Cumarin Dibrom- Monobrom-



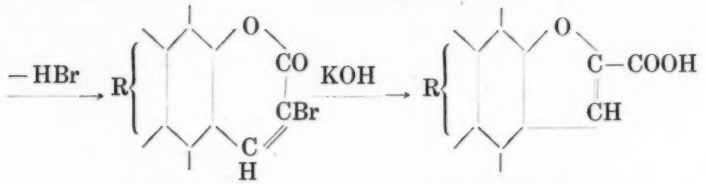
Cumarilsäure

(1) Vorläufige Mitteilung in *J. Chem. Soc. Japan*, **49** (1928), 110 u. 415.
(2) Dieses Bulletin, **4** (1929), 16.

Daher kann man die Reaktions-reihen vom Nodakenetin sehr wahrscheinlich in folgender Weise erläutern:



Nodakenetin zwisch. Prod.



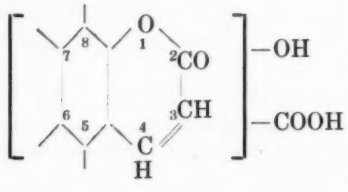
Monobrom- Nodakilsäure.

Das Monobrom-nodakenetin schmilzt bei 230-231°. Diese der Cumarilsäure entsprechende Säure wird "Nodakilsäure" bezeichnet und schmilzt bei 214–215°, es gibt durch Diazomethan eine Monomethyl-verbindung vom Schmp. 133–134°, die durch Alkali verseift werden kann.

Wegen oben erwähnter Resultate kann man also das Nodakenetin mit guten Grunde als ein Derivat der Cumarin-reihen auffassen; ja diese Ansicht kann man durch unter beschriebene Untersuchungen endgültig beweisen und auch die Konstitution des Nodakenetins grössten Teils erklären.

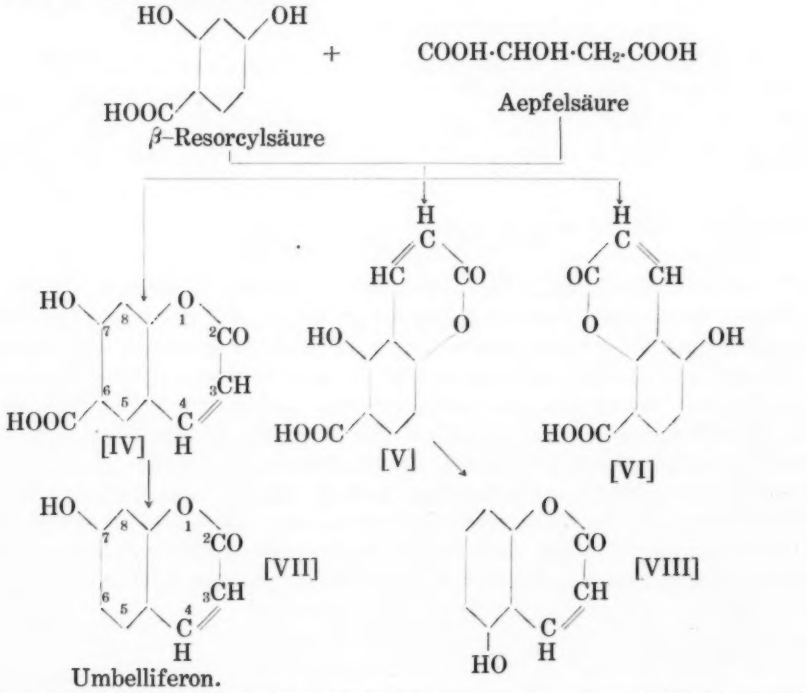
Durch Oxydation mit verd. Chromsäure gibt das Nodakenetin eine Phenolcarbonsäure, die die Formel $C_{10}H_6O_5$ mit dem Schmp. 244–246° (Zersetzt.) hat. Diese Phenolsäure ist einbasisch, enthält eine Lactongruppe, und zeigt mit Eisenchlorid eine violette Farbenreaktion wie die Salicylsäure. Und mit Diazomethan gibt es eine Dimethyl-verbindung vom Schmp. 165–166°. In Anbetracht der eben erwähnten Eigenschaften dieser Säure liegt die Vermutung sehr nahe, dass sie eine Oxycumarincarbonsäure ist und das Formelbild (IV) besitzt.

[IV]



Aber sind alle die bisher bekannten Oxy-cumarin-carbonsäuren,—7-Oxy-cumarin-carbonsäure-3[1], 7-Oxy-cumarin-carbonsäure-4[2], 6-Oxy-cumarin-carbonsäure-4[3], und 4-Oxy-cumarin-carbonsäure-3[4],—von dem vom Verfasser erhaltenen Säure entschieden verschieden. Um daher die Konstitution der Säure zu ermitteln wurden synthetische Versuche vorgenommen. Und glücklicherweise konnte der Verfasser dieselbe Oxycumarin-carbonsäure aus β-Resorcylsäure und Aepfelsäure nach Pechmannscher Methode[5] aufbauen. Die durch die Synthese erhaltene Oxy-cumarin-carbonsäure, die bei 244–246° schmilzt (Zersetzt.), stimmt mit de durch den Abbau erhaltenen vollkommen überein; auch stimmen die beiden Dimethyl-verbindunden der beider Säuren vollkommen überein, und die Mischprobe zeigt keine Depression. Die Identität beider Säuren liegt ohne Zweifel vor.

Daher muss die Oxycumarincarbonsäure nach dem Aufbau aus β-Resorcylsäure und Aepfelsäure einer der unten bezeichneten drei Formeln, (IV), (V), und (VI) entsprechen.



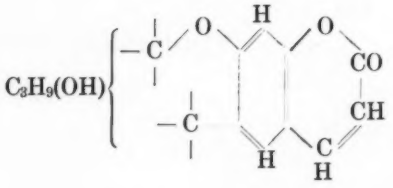
(1) H. v. Pechmann, *Ber.* **34**, 385.
(2) Ibid, 381.
(3) P. Biginelli, *Ber.* **28**, R, 155; *Gazz. Chim.* **24**, 11, 491.
(4) R. Anschutz, *Ann.* **379**, 335.
(5) H. v. Pechmann, *Ber.* **17**, 932.

Diese Oxycumarincarbonsäure wird aber durch Erhitzen über ihren Schmp. unter Abspaltung von Kohlendioxyd in eine Oxycumarin uber-geführt, das bei 230° schmilzt. Dieses Oxycumarin stimmt mit dem 7-Oxy-cumarin vom Schmp. 230–231°, das nach Pechmannscher Synthese aus Resorcin und Aepfelsäure erhalten wird, vollkommen überein, und die Mischprobe zeigt keine Depression.

Also dieses durch Decarboxylierung erhaltene Oxycumarin ist nicht anders als 7-Oxycumarin (VII) d.h. Umbelliferon.

Daher muss die Oxycumarincarbonsäure die Konstitution (IV), d. h. 7-Oxycumarin-carbonsaure-6, haben, da die anderen zwei, (V) und (VI), durch Decarboxylierung das 5-Oxy-cumarin (VIII) geben müssen.

Aus diesen Resultaten kann man schliessen, dass das Nodakenetin das Formelbild (IX) besitzen muss:



[IX]

Beschreibung der Versuche.

Brom-nodakenetin. Zu einer Lösung von 1 gr. Nodakenetin in 4 c.c. Chloroform wurden unter Kühlung 0.7 gr. Brom, das mit 2 c.c. chloroform verdünnt wurde, langsam zugetropt. Das Reaktionsgemisch, das zu einen Krystallbrei erstarrt war, gasst man in eine Schale und lässt freiwillig verdunsten, wobei sich Bromwasserstoffgas entwickelte. Der Rückstand wurde mit wenig Aether umgerührt und freiwillig verdunsten lassen, dies mehrmals wiederholt bis kein Bromwasserstoffgas sich entwickelte. Den Rückstand digeriert man mit etwas Aether, filtriert und trocknet auf der Tonplatte, und krystallisiert aus Chloroform um. Die Ausbeute ist eine fast quantitative. Es bildet farblose, prismatische Krystalle vom Schmp. 230–231°. Es ist löslich in Alkohol, unlöslich in Wasser und Aether.

Best. des Broms. 4.653 mg. Sbst.; 2.671 mg. Ag Br. Gef.: 24.41 %. Ber. für $C_{14}H_{15}O_4Br$: 24.60%.

Nodakilsaure. 1 gr. Brom-nodakenetin wurde in einer Lösung von 2 gr. Kaliumhydroxyd in 20 c.c. absol. Alkohols eingetragen. Nach dem Umschütteln wurde die Reaktionsmasse auf dem Wasserbade bis zum Sieden erhitzt und 15 Minuten im Sieden erhalten. Dabei erstarrte sie zu

einem Krystallbrei. Man verdünnte nun mit demselben Volumen Wasser und dampfte den Alkohol ab. Nach dem Erkalten wurde die Lösung mit verd. Schwefelsäure angesäuert. Die ausgeschiedenen Krystalle wurden abfiltriert und auf der Tonplatte getrocknet. Die Ausbeute betrug 0.7 gr. Es krystallisiert aus verd. Alkohol in kleinen farblosen Prismen vom Schmp. 214–215°. Es enthält kein Brom. Es ist löslich in wässerigen Alkalien und Natriumbicarbonat, die Lösungen zeigen keine Fluorescenz.

Anal. 5.332, 5.337 mg. Sbst.; 12.472, 12.571 mg. CO_2; 2.722, 2.786 mg. H_2O. Gef.: C=64.21, 63.80; H=5.71, 5.84 %. Ber. für $C_{14}H_{14}O_5$: C=64.09, H=5.38%.

Krystallwasser. 5.706, 5.711 mg. Sbst.; 0.374, 0.374 mg. H_2O. Gef.: 6.57, 6.56 %. Ber. für $C_{14}H_{14}O_5+H_2O$: 6.94 %.

Saurezahl. 7.81 mg. Sbst. (Krystallwasserhaltige); 1.35 c.c. 0.0208 N. KOH. Gef. (in Alkohol mit Phenolphtalein als Indikator): 199. Ber. für $C_{13}H_{13}O_3 \cdot COOH \cdot H_2O+1$ Mol. KOH: 200.

Es ist keine Verseifungszahl.

Nodakilsäure-methylester. 0.1 gr. gepulverte Nodakilsäure wurde in wenig Aether suspendiert und in üblicher Weise mit Diazomethan methyliert.

Der aus Aether umkrystallisierte Ester bildet farblose Prismen vom Schmp. 133–134°. Ausbeute 0.085 gr. Es ist unlöslich in kalten wässerigen Alkalien.

Best. der Methoxyls. 2.447, 2.588 mg. Sbst.; 2.007, 2.166 mg. AgJ. Gef.: 10.84, 11.06 %. Ber. für $C_{13}H_{13}O_3 \cdot COOCH_3$: 11.22%.

Mol.-Gew. 0.407 mg. Sbst. in 3.87 mg. Campher: Δ=14.4°. Gef. (Rast): 292. Ber. für $C_{15}H_{16}O_5$: 276.

Verseifungszahls. 10.08 mg. Sbst.: 1.82 c.c. 0.0191 N.KOH Verbrauch. Gef. (in 2 c.c. Alkohol 1.00 c.c. 1/10 N.KOH gelöst und auf dem Wasserbade 3 Stunden lang erhitzt, und dann mit 1/50 N.KOH rücktitriert.): 195. Ber für $C_{13}H_{13}O_3 \cdot COOCH_3+1$ Mol. KOH: 203.

Oxydation des Nodakenetins mit Chromsaure. 7-Oxy-cumarin-carbonsäure-6. Zu einer Lösung von 1 gr. Nodakenetin in 200 c.c. siedender 2% iger Schwefelsäure wurde die Lösung von 2.4 gr. Kaliumbichromat in 40 c.c. Wasser portions-weise zugefügt, und noch auf dem Sandbade 3 Stunden lang gekocht. Nach dem Erkalten wurde das ausgeschiedene, unangegriffene Nodakenetin abfiltriert. Das Filtrat wurde dreimal mit Aether geschüttelt. Die wässerige Lösung wurde mit Natronlauge alkalisch gemacht und einige Stunden stehen gelassen. Dann wurde es nochmal mit verd. Schwefelsäure angesäuert und einige Tage stehen gelassen. Dann schieden sich gelbliche Krystalle aus. Die Ausbeute betrug 0.08 gr. Beim Konzentrieren des Filtrats erhielt man nochmals 0.13 gr. Krystalle. Die aus 50% igem Alkohol umkrystallisierte Säure bildet weisse Nadeln. Die Ausbeute an reiner Säure betrug 0.15 gr.,

Schmp. 244-246° (Zersetzt), beim langsamen Erhitzen stieg der Schmp. auf 260–261° (Zersetzt). Es ist löslich in Alkohol, verd. Alkalien und Natriumbicarbonat-lösung, wenig in Wasser und Chloroform, und schwer in Aether. Die wässerige Lösung reagiert sauer und zeigt mit Eisenchlorid eine violette Farbenreaktion wie die Salicylsäure. In verd. Alkalien gibt es eine blaue Fluorescenz wie die Cumarin-reihen.

Anal. 3.826, 5.375 mg. Sbst.; 8.142, 11.507 mg. CO_2; 1.137, 1.529 mg. H_2O. Gef.: C=58.06, 58.53; H=3.33, 3.19 %. Ber. für $C_{10}H_6O_5$: C=58.27; H=2.94 %.

Krystallwasser. 4.222, 5.857 mg. Sbst.; 0.346, 0.484 mg. H_2O Gef.: 8.20, 8.25 %. Ber. für $C_{10}H_6O_5 \cdot H_2O$: 8.04 %.

Saurezahl. 5.74 mg. Sbst. (krystallwasserhaltige); 1.26 c.c. 0.0208 N. KOH Verbrauch. Gef.: 256. Ber für $C_9H_5O_3 \cdot COOH \cdot H_2O$+1 Mol. KOH.: 251.

Diese Säure enthält ein Phenolhydroxyl, aber es scheint fast keinen Einfluss auf die Titration zu haben.

Verseifungszahl. 6.03 mg. Sbst. (krystallwasserhaltige): 295 c.c. 0.0191 N. KOH Verbrauch. Gef. (wie oben): Saurezahl+Verseifungszahl=526. Ber. für $(C_8H_5O \cdot (-\overset{O}{\overset{|}{C}}O) \cdot COOH \cdot H_2O \cdot$+2 Mol. KOH: S.-Z.+V.-Z.=502. Also: Verseifungszahl=524–256=268 (Ber.: 251).

Dimethyl-7-oxy-cumarin-carbonsäure-6. (Abbauprod.) 40 mg. 7-Oxy-cumarin-carbonsäure-6 wurde mit überschüssiger, ätherischer Lösung vom Diazomethan in üblicher Weise methyliert. Das Rohprodukt wurde aus Aether-Methylalkohol umkrystallisiert. Ausbeute 25 mg. Blassgelbe Nadeln vom Schmp. 165–166°. Es ist unlöslich in verd. kalten Alkalien.

Best. der Methoxyl. 1.799 mg. Sbst.; 3.653 mg. AgJ. Gef.: 27.07 %. Ber. für $C_{10}H_4O_3 \cdot (OCH_3)_2$.: 26.50 %.

Mol.-Gew. 0.451 mg. Sbst. in 4.45 mg. Campher.: Δ=18.5°. Gef. (Rast).: 222. Ber. für $C_{12}H_{10}O_5$.: 234.

Verseifungszahl. 4.44 mg. Sbst.; 1.95 c.c. KOH (0.0191 N.) Verbrauch. Gef. (wie oben): 471. Ber. für $C_9H_7O \cdot (-\overset{O}{\overset{|}{C}}O) \cdot COOCH_3 \cdot$+2 Mol. KOH: 479.

Synthese der 7-Oxy-cumarin-carbonsaure-6. Eine innige Mischung von 10 gr. β-Resorcylsäure und 8.4 gr. Aepfelsäure in einem Rundkolben wurde mit 20 c.c. konz. Schwefelsäure übergossen und auf dem Drahtnetz rasch bis zum beginnenden Schäumen erhitzt. Entfernt man die Flamme, so vollzieht sich die Reaktion unter lebhaftem Aufschäumen und reichlicher Gasentwicklung binnen wenigen Minuten von selbst. Nach dem Abkühlen wurde die Schmelze in fünffacher Menge Eiswasser gegossen und die nach dem eintägigen Stehenlassen abgeschiedene Krystallmasse abfiltriert. Zur Entfernung von beigemengter β-Resorcylsäure wurde die auf den Tonplatten getrocknete Masse wiederholt mit etwas Aether gut gewaschen.

Das getrocknete Rohprodukt betrug 3.1 gr. Es wurde aus 50% igem Alkohol umkrystalliert. Die Ausbeute an reinen Krystallen betrug 1.8 gr. Farblose Nadeln vom Schmp. 244–246 unter Zerz., beim langsamen Erhitzten stieg der Schmp. bis auf 260–261°. Alle anderen Eigenschaften stimmen mit den der oben erwähnten Abbauprodukte überein.

Anal. 4.780 mg. Sbst.; 10.156 mg. CO_2; 1.326 mg. H_2O. Gef.: C=57.93; H=3.10 %. Ber. für $C_{10}H_6O_5$: C=58.27; H=2.94 %.

Krystallwasser. 5.200 mg. Sbst.; 0.420 mg. H_2O. Gef.: 8.08 %. Ber. für $C_{10}H_6O_5 \cdot H_2O$: 8.03 %.

Dimethyl-7-oxy-cumarin-carbonsäure-6 (synth.) 0.10 gr. synthetische Säure wurden mit Diazomethan methyliert. Aus Aether-Methylalkohol umkrystallisiert wurde die Substanz in farblosen Nadeln vom Schmp. 165–166° gewonnen.

Ausbeute 70 mg. Alle Eigenschaften der Substanz stimmen mit der durch Abbau erhaltenen Dimethyl-oxy-cumarin-carbonsäure überein, und die Mischprobe beider Verbindungen ergab keine Depression.

Best. der Methoxyl. 2.470 mg. Sbst.; 4.985 mg. AgJ. Gef.: 26.66 %. Ber. für $C_{10}H_4O_3 \cdot (OCH_3)_2$: 26.50 %.

Decarboxylierung der 7-Oxy-cumarin-carbonsäure-6. 100 mg. Oxy-cumarin-carbonsäure wurden in einer kleinem Reagenzglasse 20 Minuten lang auf 260–270° erhitzt, wobei lebhafte Kohlendioxydentwicklung eintrat. Nach dem Abkühlen wurde die Schmelze mit Alkohol extrahiert. Das Filtrat wurde auf dem Wasserbade eingedampft und der Rückstand mit Aether extrahiert. Der Aether des Filtrats wurde verdampft und die zurückgebliebenen Krystalle wurden aus Wasser unter Zusatz von Tierkohle umkrystallisiert. Ausbeute 25 mg. Der Schmp. 230°.

Anal. 5.253 mg. Sbst.; 12.757 mg. CO_2; 1.919 mg. H_2O. Gef.: C=66.23; H=4.09 %. Ber. für $C_9H_6O_3$: C=66.64; H=3.74 %.

Diese Substanz stimmt mit dem Umbelliferon ganz überein, das nach der Pechmannschen Synthese[1] aus Resorcin und Aepfelsäure gewonnen wirde und den Schmp. 231°[2] hat. Und die Mischprobe der beiden Substanzen zeigt keine Erniedrigung.

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(1) *Ber.* **17**, 932.

(2) Nach der Literatur ist der Schmp. des Umbelliferons 225°, aber mein Substanz, dreimal aus Alkohol, nacher noch einigemal aus Wasser umkrystallisiert, schmilzt bei 231° (unkor.).

STUDIES ON THE COAGULATION OF VON WEIMARN'S Au_F—SOLS. I.

By Eiichi IWASE.

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I. Introduction. The application of P. P. von Weimarn's[1] modification of the "formaldehyde method" makes it possible to produce large amounts of dispersoidal gold solutions of a *beautiful red* colour, which are *always reproducible*; the obtaining of dispersoidal gold solutions by this modification of the formaldehyde method, may be performed in laboratories possessing no expensive equipment; that is to say, without the use of gold condensers for the distillation of water, or of beakers of extra resistant glass, etc.

Of course, in spite of their all possessing the same beautiful red colour when observed with the naked eye, the quantitative properties of these dispersoidal gold solutions are dependent upon the conditions of their preparation; e.g. the coagulation values of these red dispersoidal solutions should vary more or less considerably, in accordance with the conditions of experimenting.

Prof. P. P. von Weimarn suggested to me[2] a systematic investigation of the coagulation phenomena in dispersoidal gold solutions, obtained by his method. The programme of this investigation comprises the elucidation of the influence upon the coagulation values for various electrolytes, of the following variables: 1). Of unreduced gold compounds; 2). Of the excess of KOH and K_2CO_3 in the solution; 3). Of water different in purity; 4). Of the materials the vessels are made of; 5). Of the purity of the reagents, and especially of the formaldehyde solutions (redistilled and non-redistilled formaldehyde, its age, etc.) etc.

I wish also to express here to Prof. P.P. von Weimarn my sincere gratitude for giving me the theme of this investigation; in this brief paper are presented certain of the results obtained by me, of the coagulation values for NaCl and $BaCl_2$.

II. The Dispersoidal Gold Solutions were Prepared in Beakers of Ordinary Laboratory Glass A, with Ordinary Distilled Water; The Measuring Vessels Used were of Ordinary Laboratory Glass C. In the same

(1) P.P. von Weimarn, *Kolloid-Z.*, **33** (1923) 74 & 228; **36** (1925) 1; **39** (1926) 166 & 278; **45** (1928), 203 & 366. This Bulletin, **4** (1929), 34. *Japanese Journal of Chemistry*, **3** (1929), 165.

(2) P.P. von Weimarn, *Japanese Journal of Chemistry*, **3** (1929), 201.

Room, Simultaneously with the Dispersoidal Gold Synthesis, were Carried out Other Chemical Experiments.[1] Dispersoidal solution "Sol B_1" was obtained by boiling a mixture of 500 c.c. distilled water (20°C.) + 10 c.c. $AuCl_3HCl4H_2O$-solution (0.6%) + 3.5 c.c. reagent $F^{10}_{0.2KOH}$. Immediately after the beginning of boiling (it required about 10 minutes' heating) into this mixture were poured, in portions, 150 c.c. distilled water. After about 30 minutes' boiling, the volume of the solution equalled 500 c.c. (at room temperature). The $AuCl_3HCl4H_2O$ and KOH were *extra pure*. The formaldehyde solution was *redistilled*.

In Table 1 are given data of *one* experiment with NaCl (*extra pure*) and in Table 2 of *one* experiment with $BaCl_2$ (*extra pure*).

Table 1. "Sol B_1."

Concentration of NaCl per litre (in millimols): / Colour of sol:	12	14	17	19	22	24	26
at the time of addition:	red	red	red	red	violet-tish-red	violet-tish-red	violet-tish-red
after 5 min.	red	red	red	violet-tish-red	violet-tish-red	violet-tish-red	*violet.*
after 15 min.	red	red	red with a violet tinge	reddish-violet	reddish-violet	reddish-violet	violet.
after 2 hours:	red	red	red with a violet tinge	reddish-violet	violet	violet	turbid, the intensity of colour falls off.
after 20 hours:	red	red	red with a violet tinge	*violet.*	*violet slightly turbid.*	the intensity of colour falls off markedly	almost colourless.

(1) Glass C is more sensitive to a weak solution of alkalies than is glass A; see P.P. von Weimarn, l.c. The determination of the coagulation values was always carried out in a separate room, which was heated by electricity and in which no other chemical work was performed. The NaCl and $BaCl_2$-, KOH- and $AuCl_3HCl4H_2O$- solutions were prepared with water, redistilled through Jena glass.

Table 2. "Sol B_1."

Concentration of $BaCl_2$ per litre (in millimols): / Colour of sol:	0.06	0.09	0.11	0.14	0.16–0.17	0.18
at the time of addition:	red	red	red	red	red	violettish-red
after 5 min.	red	red	red with a violet tinge	violettish-red	*violet*	violet
after 15 min.	red	red	red with a violet tinge	violettish-red	violet.	violet
after 2 hours:	red	red	violettish-red	violet with a red nuance	violet	the intensity of colour falls off, the sol is slightly turbid
after 20 hours:	red	red	violettish-red	*violet*	*violet, slightly turbid.*	almost colourless.

In Tables 3 and 4 are shown similar data for "Sol B_1+150 c.c. KOH, 0.02 norm.; the method of preparation of this sol was quite similar to that of "Sol B_1," the only difference being that, instead of 150 c.c. distilled water, there were added, for a more complete reduction, 150 c.c. of KOH-solution, 0.02 norm. *extra pure.*

Table 3. "Sol B_1+150 c.c. KOH, 0.02 norm."

Concentration of NaCl per litre (in millimols): / Colour of sol:	4	5	7	10	12	14	16
at the time of addition:	red	red	red	red	red	red with a violet tinge	red with a violet tinge
after 5 min.	red	red	red	red	red with a violet tinge.	violet-tish-red	*violet.*
after 15 min.	red	red	red with a violet tinge	violet-tish-red	reddish-violet	reddish-violet	violet
after 2 hours:	red	red	red with a violet tinge	reddish-violet	violet	violet	violet
after 20 hours:	red	red with a violet nuance	violet-tish-red.	*violet.*	violet	*violet, turbid,*	the intensity of colour falls off, the sol is turbid.

Table 4. "Sol B_1+150 c.c. KOH, 0.02 norm.

Concentration of $BaCl_2$ per litre (in millimols): / Colour of sol:	0.006	0.011	0.016	0.021	0.026	0.030	0.035
at the time of addition:	red	red	red	red	red	red	red
after 5 min.	red	red	red	red	red	violettish-red	*violet*
after 15 min.	red	red	red	red with a violet tinge	violettish-red	violet	violet
after 2 hours:	red	red with a violet tinge	red with a violet tinge	reddish-violet	violet	violet	violet
after 20 hours:	red	*violet.*	violet	violet	*violet, slightly turbid.*	violet, turbid	almost colourless.

In Table 5 are summed up the results of different experiment (by I, II, III, and IV are designated dispersoidal gold solutions prepared at different times; by a, b and c are designated the coagulation values for different portions of one and the same dispersoidal gold solution).

Table 5. (Red→violet after 5 minutes).

	"Sol B_1"		"Sol B_1+150 c.c. KOH, 0.02 norm."	
	NaCl	$BaCl_2$	NaCl	$BaCl_2$
I	27	0.16	a. 16, b. 16	0.03
II	a. 26, b. 26	0.16	a. 16, b. 16	between 0.03–0.035
III	a. 28, b. 28	a. 0.18, b. 0.17, c. 0.17	a. 16, b. 16	between 0.03–0.035
IV	—	—	—	0.04
Mean	27	0.17	16	0.03

III. The Dispersoidal Gold Solutions were Prepared with Ordinary Distilled Water, in Beakers of Glass A; the Measuring Vessels were of Jena Glass and of Glass A; no Other Chemical Experiments were Performed in the Room. Under these conditions, the intensity of colour (at room temperature), of "Sol B_1+150 c.c. KOH. 0.02 norm." when compared with "Sol B_1," showed a much smaller increase, than in similar experiments described in Section II.

Table 6. (Red→violet after 5 minutes).

	"Sol B_1"		"Sol B_1+150 c.c. KOH, 0.02 norm."	
	NaCl	$BaCl_2$	NaCl	$BaCl_2$
I	between 27–28	0.21	19	0.06
II	——	——	17	0.06
III	——	——	19	0.08
Mean	27.5	0.21	18	0.07

In Table 6 are summed up the data, pertaining to the coagulation values for NaCl and $BaCl_2$; these values are considerably greater than those obtained in dispersoidal synthesis carried out in a room where other chemical experiments are being performed at the same time, and with measuring vessels made of glass C, which is more sensitive to weak solutions of alkalies.

IV. The Dispersoidal Gold Solutions were Prepared in Beakers of Jena Glass, with Water Redistilled Through a Condenser of Jena Glass.

Table 7. (Red→violet after 5 minutes).

	"Sol B_1".		"Sol B_1+150 c.c. KOH, 0.02 norm."	
	NaCl	$BaCl_2$	NaCl	$BaCl_2$
I	between 24–25	between 0.17–0.18	13	0.03
II	25	0.18	a. 14, b. 14	0.03
III	a. 24, b. 24	0.17	——	——
Mean	24	0.17	14	0.03

From the data given in Table 7, it is clearly seen that the coagulation values for NaCl and $BaCl_2$ are *not* increased by using, instead of ordinary distilled water, water redistilled through a Jena glass condenser, nor are they by using Jena glass beakers, instead of those made of glass A.

V. Conclusion. The above coagulation numbers for NaCl and $BaCl_2$ admit of the following conclusions:

A. By varying the conditions of obtaining "Sol B_1," the coagulation values are changed relatively little; for NaCl the changes are within the limits of 27.5 and 24, or 14 per cent, and for $BaCl_2$, between 0.21 and 0.17, or 23 per cent.

B. By varying the conditions of obtaining "Sol B_1+150 KOH, 0.02 norm.," the coagulation values become changed considerably; viz. for NaCl they are between 18 and 14, or 28 per cent. For $BaCl_2$ the changes in coagulation values are very great; they are expressed between 0.03 and 0.07, or 133 per cent.

C. The greatest difference in the coagulation values for "Sol B_1" and "Sol B_1+150 c.c. KOH, 0.02 norm.," is for NaCl between 27.5 and 14, a difference of 96 per cent; and for Ba Cl_2 between 0.21 and 0.03, a difference of 600 per cent.

D. Dispersoidal solutions "Sol B_1+150 c.c. KOH, 0.02 norm." although the difference in their coagulation values for $BaCl_2$ rises up to 600 per cent. preserve their *pure red* colouring; only the colour becomes darker (more intense) and the brownish opalescence in reflected light increases. Other conditions being equal, the darker the red colour, and the stronger the opalescence, the less is the coagulation value for $BaCl_2$.

I shall devote my future papers to the consideration of the influence of separate variables upon the coagulation values, now I wish only to point out that the intensity of the red colour of "Sol B_1+150 c.c. KOH, 0.02 norm." prepared in a gold beaker, with water redistilled through a gold condenser, differs very little from that of "Sol B_1" (prepared also in a gold beaker and with the same *extra pure* water); in this case, the coagulation numbers of "Sol B_1+150 c.c. KOH, 0.02 norm.," for NaCl are 20 and for $BaCl_2$, 0.08.

In conclusion, I wish to extend my hearty thanks to Prof. P. P. von Weimarn for kindly guiding me into the world of Dispersoidology, during my stay in his laboratory, from September 1926 to April 1929.

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SORPTION OF GAS BY THE POROUS MATTER.

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Sorption of the gases by the porous matters such as charcoal, silica gel etc. are generally considered to be one of the adsorption phenomena. Thus the molecules of the gas condense on the surface of the charcoal. Some authors consider that the gas molecules condense to liquid in the capillary. But it is highly improbable that, except the easily condensable

vapours, the gas liquefies at a temperature so appart from its normal boiling point. McBain considered that a small part of the gas diffuse into the mass of charcoal while the most part are adsorbed on the surface of the charcoal, and he used the term "sorption" for such a case.[1]

The author measured the sorption amount by various kinds of charcoals of air[2] and of carbon dioxide as well as the sorption velocity by sugar charcoal of carbon dioxide.[3] It was known that the sorption velocity of gas by the granular charcoal is smaller than that by the powder one, while the sorption amounts by both charcoals are quite the same. We saw, moreover, that the amounts of sorptions of carbon dioxide by various kinds of charcoals are not so different each other notwithstanding the divergence of the materials from which the charcoals were made. According to the results of these observations, the author concluded that the sorption of gas by charcoal is to be ascribed to the dissolution and not to the adsorption.

By the experiments of the sorption of gases by chabazite,[4] it can naturally be supposed that the gas molecules enter into the crystal of the dehydrated chabazite in the places where the water molecules has formerly situated. There are vacant cavities in the dehydrated chabazite crystal, each of which was formerly filled with water molecule. If such dehydrated chabazite is brought in contact with gas, the gas molecules enter into the mass of the crystal and take possession of the cavities which were left unoccupied. Thus the crystal is still a homogeneous phase in the sence used in phase rule.

The author consider that the same can be said in the case of charcoal and silica gel. Charcoal has a great number of molecular cavities which were left when it was produced by the decomposition of carbohydrate etc. Silica gel has also molecular cavities left by the departure of water molecules in the process of dehydration.

Now the gas molecule dash into one of these molecular cavities and it is attracted and captured by the surrounding charcoal atoms or silica molecules. The gas molecule settles into the molecular cavity and make a homogenous solid solution. So the sorption process is not quite the same with the ordinary dissolution process, while the product is a solid solution. The phenomena neither be called "absorption" nor "adsorption." We will use the term "sorption" for this case, having the different meaning

(1) McBain, *Z. physik. Chem.*, **68** (1909), 471.
(2) Sameshima and Hayashi, *Science Reports of the Tohoku Imperial University*, **12** (1924), 289.
(3) Sameshima, this Bulletin, **2** (1927), 1.
(4) Sameshima, this Bulletin, **4** (1929), 96.

from that used by McBain. Our " sorption " means the entering of the gas molecule into the molecular cavities and forming a solid solution.

It is well known fact that the more easily condensable gas are sorped the more, and this is considered to be one of the reasons of the adsorption hypothesis. This relation, however, hold never strictly but only approximately. According to the author's theory, the easily condensable gas molecule is liable to be captured more easily than the non-condensable gas molecule. In other words, the more active gas molecule is the more difficult to be prisoned. In the process of the ordinary dissolution, the solute molecule push aside the solvent molecules, or the solvent molecules make room for the solute molecule. So the molecular affinity between solute and solvent molecules is the most important factor for the ordinary dissolution.

Some authors describe that the rapidity of sorption of gases by the porous matters is to be due to the surface adsorption. They said that if it be a diffusion phenomena, then the sorption will proceed more slowly.[1] This statement is correct, however, only in the case of the diffusion into a compact solid body. In a case of the porous body such as charcoal, the contact surface between gas and solid is very large, and therefore, the "diffusion" goes on very rapid. By powdering the charcoal, the surface area will increase so the sorption velocity will also increase. This was already proved experimentally.[2]

Other reason of the adsorption hypothesis consists in the non-expansion of the adsorbent body. The expansions of charcoals by the sorptions of carbon dioxide and water vapour are observed recently by Meehan,[3] and Bangham and Fakhoury.[4] The amounts of expansions of charcoals determined by these authors are rather small, i.e. in the order of 0.1%. This can be explained by the present author's theory that the CO_2 molecules enter into the cavities of charcoal.

It is known that the sorption isotherm generally deviates from the Henry's law. This can easily be understood from the difference between the author's theory and the ordinary dissolution process. In the case of the sorption of hydrogen by charcoal, the Henry's law is applicable.[5] Recently, Magnus and co-workers[6] have determined the sorption isotherms by purified charcoal and silica gel of carbon dioxide at low pressures and known that the Henry's law is applicable.

(1) Zsigmondy, " Kolloidchemie," 4ed. (1924), p. 85.
(2) Sameshima, this Bulletin, **2** (1927), 1.
(3) Meehan, *Proc. Roy. Soc.* (London), A, **115** (1927), 199.
(4) Bangham and Fakhoury, *Nature*, **122** (1928), 681.
(5) Titoff, *Z. physik. Chem.*, **74** (1910), 641.
(6) Magnus and co-workers, *Z. anorg. allg. Chem.*, **174** (1928), 142; **179** (1929), 215.

Summary.

The mechanism of the sorptions of gases by charcoal, silica gel and chabazite etc. are discussed. The author's theory for these cases is as follows: The gas molecules enter into the molecular cavities in the solid body and form a homogeneous solid solution.

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